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User's Guide to Model for Aquatic Chemical Speciation Software Package: MACS80 (Version 5/1990-VAX and MS-DOS®) 3rd edition

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Central and Arctic Region
Department of Fisheries and Oceans
Winnipeg, Manitoba R3T 2N6

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This is the 44th Technical Report

from the Central and Arctic Region

ERRATA

Wagemann, R., and G. Regehr. 1992. User's guide to model for aquatic chemical speciation software package: MACS80 (Version 5/1990-VAX and MS-DOS®). 3rd edition. Can. Tech. Rep. Fish. Aquat. Sci. 1848: iv + 41 p.

Page 5, Manganese line: columns 2,3 and 4 are misaligned. The "10" after "Manganese" should be in column 2, and "0.01" "MG/L" should be in columns 3 and 4 respectively.

Page 9, Solid Number 15: the formula should read $Mg_4(PO_4)_3H$.

Page 17, Quadratic Coefficient Test, quadratic equation formula: the square root should encompass both terms i.e.

$$\sqrt{b^2-4ac}$$

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ABSTRACT

Wagemann, R., and G. Regehr. 1992. User's guide to model for aquatic chemical speciation software package: MACS80 (Version 5/1990-VAX and MS-DOS®). 3rd edition. Can. Tech. Rep. Fish. Aquat. Sci. 1848:iv+41 p.

The manual is a guide to running the MACS80 chemical speciation program. The program calculates the equilibrium concentration of chemical species as a function of pH in fresh water aquatic systems from the given total dissolved concentration of metals and anions either in the presence or absence of one or more of over sixty solids. It takes into account fifteen anions and fourteen metals commonly found in fresh waters including the interaction of metals (Cu, Cd) with humic dissolved substances and the adsorption of cadmium on suspended particulate matter. The program provides the option of performing these calculations on a closed or open system with respect to atmospheric carbon dioxide. A step by step description of the various input requirements and output options is given. The program can calculate results at different temperatures. The manual provides an overview of the algorithm including flow-charts and explains the process of how results are calculated, their precision and dependence on temperature in terms of equilibrium constants and activity coefficients. The manual also provides some guidance to programmers on how to expand the program to encompass a larger number of metals and anions.

Key words: computer programs; algorithms; chemical speciation; fresh water; cadmium.

RÉSUMÉ

Wagemann, R., and G. Regehr. 1992. User's guide to model for aquatic chemical speciation software package: MACS80 (Version 5/1990-VAX and MS-DOS®). 3rd edition. Can. Tech. Rep. Fish. Aquat. Sci. 1848:iv+41 p.

Le manuel est un guide d'exploitation du programme de détermination des espèces chimiques MACS80. Ce programme permet le calcul de la concentration à l'équilibre d'espèces chimiques en fonction du pH dans des systèmes d'eau douce à partir de la concentration totale en métaux dissous et en anions, en présence ou non d'une ou plusieurs matières solides parmi soixante. Le programme tient compte de quinze anions et quatorze métaux communément trouvés en eau douce, ainsi que des interactions de métaux (Cu, Cd) avec des substances humiques dissoutes, et de l'adsorption du cadmium sur les particules en suspension. Le programme offre la possibilité d'effectuer ces calculs en système fermé ou en système ouvert, avec le gaz carbonique atmosphérique. Une description des différents paramètres d'entrée et des options de présentation des résultats est fournie. Le programme peut calculer les résultats à différentes températures. Le manuel donne un aperçu de l'algorithme, notamment avec des graphiques de cheminement, et il explique de quelle façon les résultats sont calculés, indique leur précision ainsi que leur dépendance par rapport à la température en termes de constantes d'équilibre et de coefficients d'activité. Le manuel fournit en outre quelques éléments à l'intention des programmateurs sur la façon d'élargir le programme de manière à incorporer un nombre accru de métaux et d'anions.

Mots clés: programmes d'ordinateur; algorithmes; détermination d'espèces chimiques; eau douce; cadmium.

1.0 ACKNOWLEDGMENTS AND OVERVIEW

The MACS80 speciation program has an extensive history of development, becoming, through necessity, larger and more complex at each stage. We sincerely thank Messrs. D. Abrams, W. Elliot, M. Judd, D. Bayomi and R. Lypka for their programming contributions at various stages of development. We particularly thank Mr. D. Abrams who was the first to undertake the programming task, and Mr. D. Costin (Head of the Freshwater Institute Computer Section at that time) for their cooperation and generosity with their time. We also thank Ms. P.V. Cassidy for typing. One of us (G. Regehr) adapted, modified and enhanced the program for use on a MICRO VAX II computer, as well as microcomputers under MS-DOS®.

1.1 OVERVIEW

This manual is intended only to facilitate the use of the program, explain its various options, and provide a brief description of the algorithm. The source code for the program has been published separately (Wagemann et al. 1990). The data base used by this program will be published as a separate compilation of equilibrium constants with their sources and the corresponding chemical equations. However, the user can obtain a hard copy of the equilibrium constants and activity coefficients used by the program as explained later (see section 2.2.2 10)). The equations used in this program and referred to in this manual can be found in any physical chemistry text. The equilibrium constants used by this program have been obtained, whenever possible, from a critically assessed compendium of constants (Smith and Martell 1976).

To verify the validity of the calculations as such, a published standard river water data set was used as the input and the calculated results were compared with the published results from 14 other well-known speciation programs using the same input (Jenne 1979). The results obtained by this program were comparable to those obtained by the other programs that had the temperature variation option as this programs has. Nevertheless, there are numerous modelling pitfalls which can be more or less severe depending on the type of aquatic system being analysed and the specific aim of these calculations. The user must have some knowledge of physical chemistry to be able to properly assess the significance or insignificance of the shortcomings of chemical modelling in general, in relation to the particular aquatic system being analysed in particular, and in relation to the specific goals under consideration. The ease of use of the program cannot absolve the user from excercising enlightened caution in the interpretation of results based on some understanding of ion associations, ion activity, ionic strength, thermodynamic constants, chemical equilibria, chemical kinetics, metastable equilibria, and the limitations that these concepts may impose to a greater or lesser degree on the results. Equally important is an understanding of what constitutes an appropriate definition of the physico-chemical system in relation to the goals sought. The situation is not unlike that engendered by the availability of very "user-friendly" statistical programs where results can be obtained easily and quickly even by novices but the correct assessment and interpretation of results still requires an understanding of the subject matter.

The program MACS80 (Model for

Aquatic Chemical Speciation - 1980) is designed to calculate the concentration of chemical species in equilibrated freshwater systems. It requires the specification of parameters, such as the total dissolved concentration of chemical species in the aquatic system. The program can generate different reports by allowing the user to define outputs for specific metals and anions. Since the program requires the use of only one input file and performs all of the input, error-checking, calculations and report generation without auxiliary programs, it is relatively simple and straight-forward to use.

The input for the program consists of a definition of the physical system and a specification of the total dissolved concentration of the main species or elements.

The program is available in versions compiled under VAX FORTRAN 77 to run on a MICRO-VAX II and under Microsoft FORTRAN Version 5 to run on MS-DOS® computers. Differences between the two versions are minor, consisting mainly of different file naming conventions (e.g. MACS80.INPUT for the VAX and MACS80.INP for MS-DOS®). The source code for the MS-DOS® version has been published (Wagemann et al. 1990). Source code and executables for both versions are available from the authors.

The algorithm of the MACS80 program is based on the equilibrium and mass balance approach, resulting in a set of polynomial equations. The coefficients of the terms in these equations are stored in a three-dimensional array (APPENDIX III). The coefficients are indexed by the anion, metal, and the power of the term in the equation (i.e., linear, quadratic, cubic; see sections 8.3 and 10.1). This program is easily expanded by enlarging the array that contains the terms of the coefficients and by adding the necessary equilibrium constants. The basic principle underlying this approach is that the chemical equations are expressed for each ion as a polynomial, and the solutions are provided by the positive roots of the polynomial. The program can and does deal with mixed ligand complexes and can calculate the concentration of such mixed ligand species.

1.2 NARRATIVE

The program starts computing by reading in from a separate input file (MACS80.INPUT or MACS80.INP for the microcomputer) a set of chemical and physical parameter values which defines the aquatic system. All parameters must be specified in this input file. If a total dissolved concentration of an anion or metal is not specified, it is set to zero by default and the calculation proceeds on that basis. No "seed" values or guessed starting values need be entered to start the calculation. The program itself generates the appropriate starting values for all the variables.

If there is an error on input in the parameter sets, the system is not analyzed nor are any reports printed. The program prints out an error message and stops. If there are no errors in the set of input parameters, the program proceeds to analyze the system.

The species concentrations are calculated (equilibrium conditions are assumed) by the solution of the polynomial equations by iteration between the anion/metal mass-balance equations, and utilizing the initial inputs of total concentrations of anions and metals, and the physical input parameters defining the aquatic system. The program calculates the concentration of each species at each pH

increment in the specified pH range. For the actual processing of the analysis see section 8.3. If the calculations do not converge after 100 reiterations the analysis is stopped, no reports are written for this pH value and an error message is written. If there are no positive roots (i.e., negative concentration) or the concentration of a particular species is approaching zero, then the concentration is set to 0.

When the computation is completed, the program prints out the reports requested.

2.0 FILE INFORMATION

2.1 PROGRAM FILE

The directory MACS contains the file MACS80.EXE, which is the executable program file. The source file exists as MACS80.FOR. Updating of the source can be done through the VAX editor EVE or any other compatible ASCII editor. The source must then be recompiled and linked to generate a new executable program.

The program is executed under VMS by entering the command RUN MACS80 or under DOS® by entering MACS80 after entering data into the input file MACS80.INPUT (or MACS80.INP) (see Table 1) which must be present in the MACS directory.

Table 1. Data input file "MACS80.INPUT or MACS80.INP"

TITLE	LAKE 382 AT EP, July 18, 1991. RUN 20C	
TEMPERATURE	20.0	
PCO2	.000350 CONTROLS T.D. IC=T	
IONIC STRENGTH	0.0036	
CONDUCTIVITY	24.0	
pH RANGE	MIN=4.5 MAX=8.1 INC=0.2	
pH SPECIFIC		
SEDIMENT CD CONSTANT =	3.18660D-9 *10^(1.1593 * PH)	
OUTPUT UNITS:	MOLES/L	MG/L
CONCENTRATION	F	F
LOG(CONC)	F	F
%(CONC)	F	T
DEFINITIONS	F	

Table 1. continued: ANION and METAL parameters.

O2UTPUT FILE	>MACS<	ID	>R20C<		SOLID	REPORT	FILENAME
A SULFATE		2	3.3	MG/L	00	F	> <
A EDTA		3	0	MG/L	00	F	> <
A NTA		4	0	MG/L	00	F	> <
A INORGANIC CARBON		5	9.1D-5	MOLES/L		T	>IC <
A CHLORIDE		6	0.3	MG/L	00	F	> <
A ORGANIC CARBON		7	7.2066	MG/L	00	T	>OC <
A SELENITE		8	2D-4	MG/L	00	F	> <
A SILICATE		9	0.527	MG/L	00	F	> <
A AMMONIA		10	0.112	MG/L	00	F	> <
A ORTHO-PHOSPHATE		11	2D-3	MG/L	00	T	>OP <
A ACETATE		12	0	MG/L	00	F	> <
A SULFIDE		13	0.0D-2	MG/L	00	F	> <
A SEDIMENT		14	2.0	MG/L	00	T	>SED <
A FLUORIDE		15	0.0	MG/L	00	F	> <
M SODIUM		1	0.95	MG/L	00	F	> <
M MAGNESIUM		2	0.66	MG/L	00	F	> <
M CALCIUM		3	2.11	MG/L	00	F	> <
M IRON(III)		4	0.040	MG/L	00	F	> <
M MERCURY(I)		5	0	MG/L	00	F	> <
M MERCURY(II)		6	1D-5	MG/L	00	F	> <
M CADMIUM		7	1D-4	MG/L	07	T	>CD <
M COPPER		8	2D-3	MG/L	00	F	>CU <
M IRON(II)		9	0	MG/L	00	F	> <
M MANGANESE(II)	10	0.01	MG/L		00	F	> <
M ZINC		11	1.5D-3	MG/L	00	F	> <
M POTASSIUM		12	0.44	MG/L	00	F	> <
M COBALT		13	0	MG/L	00	F	> <
M ALUMINIUM		14	0.04	MG/L	00	F	> <

2.2 DATA INPUT FILE

The input file (Table 1) is called MACS80.INPUT (MACS80.INP under DOS*) and can be edited directly using any ASCII editor.

2.2.1 Input procedure and specifications

Data input is done through the separate input file (MACS80.INPUT; or MACS80.INP) containing system parameters and options for units and reports. The layout of the input file (Table 1) is inflexible and the data must be typed into the designated fields. When values are changed, their positions in the file must remain constant. Records for metal or anion concentrations may be re-arranged or deleted, however removing a species from consideration is more easily done by setting its concentration to zero in the specified field or leaving the particular field empty, in which case a zero concentration for that ion is assumed by the program.

2.2.2 Model parameters and options

A variety of model or system parameters and report generation options may be specified. A brief description of these follows; for a description of the associated record formats, consult APPENDIX I.

1) TITLE Parameter:
A record containing this parameter marks the start of the file. The actual parameter consists of a title to be printed in the "ENVIRONMENT:" heading of the reports.

2) TEMPERATURE Parameter:
Since the equilibrium constants and activity coefficients are temperature dependent, the desired temperature may be specified for these calculations. If no temperature is specified, the calculations are automatically performed for the derfault setting, namely 25° C.

3) pCO_2 Parameter:
When this parameter is set to true i.e. "CONTROLS T.D.IC = T", the total dissolved inorganic carbon in the system is determined by equilibration with atmospheric CO_2 at any pH. Any value entered under "INORGANIC CARBON" (Table 1) is then ignored. When this parameter is reset to "CONTROLS T.D.IC = F", the given pCO_2 value is ignored, and the program uses the specified total dissolved inorganic carbon concentration entered under "INORGANIC CARBON". The pCO_2 value must be entered in units of atmospheres; in the example in Table 1, $0.00035 = 3.5 \times 10^{-4}$ Atm.

4) IONIC STRENGTH Parameter:
This parameter defines the ionic strength of the aquatic system (moles/L) and is used to calculate activity coefficients. If, in addition, the CONDUCTIVITY parameter is also specified, the program will use the given ionic strength and will omit the calculation of ionic strength from conductivity.

5) CONDUCTIVITY Parameter:
This parameter defines the conductivity of the system in terms of μSiemens/cm and is used to calculate the ionic strength if the latter is not specified. If the ionic strength is specified, this parameter is ignored.

6) pH RANGE Parameters:
These specify the pH range over which species calculations (at each pH increment) are to be performed. The range is given by minimum, maximum and pH increment

values and may be adjusted automatically by the program if the size of the range is not divisible by the increment. Up to 41 pH increments may be accommodated within any given range, i.e. [(pHMAX - pHMIN) / pHINC] + 1 < 41.
Note: If the minimum value is specified, the maximum value and increment must also be specified and vice versa.

7) pH SPECIFIC Parameter:
By specifying this parameter and omitting specifying the pH range, reports can be obtained for a single pH value only, namely the specified pH. If a pH range is also specified, reports will be obtained at each pH increment over the entire pH range, followed by the report for the specific pH, even if the specific pH value is within the pH range.

8) SEDIMENT CD CONSTANT
A major application of the program pertained to whole-lake cadmium experiments where suspended matter was found to scavange much of the added cadmium. The partition coefficent for this particular suspended matter and lake water was determined. The program takes therefore full account of the interaction between suspended matter and cadmium but does not currently have the same capability with respect to other ions. Because the adsorptive capacity of suspended matter for cadmium can vary from system to system and the variation is a function of pH, suspended matter is hitherto treated in the program individually rather than generally. Provision has therefore been made for the user to specify a different partition coefficient from that presently in the program together with different constants "a" and "b" in the exponential function "$a*10^{b*pH}$" as shown in the example input (Table 1). (No other constant can be similarly specified by the user without modification of the source code.)

9) OUTPUT UNITS Options:
Reports can be obtained in terms of concentration, log of concentration, or percentage of total dissolved concentration, each for either moles/l or mg/l units depending on which of the six options are selected by placing a 'T' (for true) in the required position.

10) DEFINITIONS Option:
Setting this option to true will cause the program to print a report of the numerical values of the equilibrium constants, activity coefficients, γ-coefficients, C values and solid numbers which identify the type of solid.

11) ANION and METAL Parameters:
These parameters represent the concentration (moles/litre or mg/L) of total anions and metals in the aquatic system which must be specified (Table 1), and are used to calculate the concentrations of the various free ions and complexes. Also, various solids in equilibrium with solution may be specified here under the "SOLID" column (as a number, see Table 2) which then determines the "free" metal or anion concentrations in solution in equilibrium with each solid. When a "SOLID", two digit, number is entered after the anion of that solid the total anion concentration in solution is allowed to vary as a function of pH i.e., the system is open with respect to that anion and the corresponding metal concentration is held constant over the entire pH range. When the "SOLID" number is entered after the metal of that solid, that total metal concentration in solution is allowed to vary with pH in order to maintain equilibrium

between solid and solution and the metal ion at all pH values and the anion concentration is held constant.

The species concentrations are calculated in the presence of as many solids as are specified, but the same solid cannot be entered at the same time under both the cation and the anion positions, since this would make the system indeterminate.

A "species report" for any particular metal or anion is obtained by entering a "T" (for true) on the appropriate line in the "REPORT" column (Table 1). The species report may also be output to a separate text file (as input for a plotting program) by filling in the filename parameter in the "FILENAME" column consisting of at most 3 characters. The 4 characters (at most) entered in the "ID" field make up the rest of the file name (See section 3 for a description of reports available).

Table 2. Listing of solids and their numbers.

Solid Number	Chemical Formula	Mineral Name
1	$Cd(OH)_2$	
2	CuO	Tenorite
3	$Cu(OH)_2$	
4	$Cu_4SO_4(OH)_6$	Brochantite
5	$MgCa(CO_3)_2$	Dolomite
6	$CaCo_3$	Calcite
7	$CdCO_3$	
8	$CuCO_3$	
9	$Cu_2CO_3(OH)_2$	Malachite
10	$Cu_3(CO_3)_2(OH)_2$	Azurite
11	$Cu_2Cl_2(OH)^3$	Atacamite
12	$Mg_5(PO_4)_3OH$	
13	$MgH(PO_4)$	
14	$Mg_3(PO_4)_2(8H_2O)$	
15	$Mg_4(PO_3)_3H$	
16	$Ca_5(PO_4)_3OH$	
17	$CaHPO_4$	
18	$Ca_3(PO_4)_2$	
19	$Ca_4(PO_4)_3H$	
20	$Cd_3(PO_4)_2$	
21	$Cu_3(PO_4)_2$	
22	CdS	
23	CuS	Covellite
24	FeS	Mackinawite
25	$Fe(OH)_2$	
26	$Fe_3(PO_4)_2(8H_2O)$	Vivianite
27	$FeCO_3$	Siderite
28	HgO	Montroydite
29	HgS (red)	Cinnabar
30	HgS (black)	Metacinnabar
31	$HgSeO_3$	
32	$CuSeO_3(2H_2O)$	Chalcomenite
33	$MgSeO_3$	
34	$Mg_2(HSiO_4)_3$	
35	$Mn(OH)_2$	
36	$MnCO_3$	
37	MnS (pink)	
38	MnS (green)	

Table 2. (Cont'd)

Solid Number	Chemical Formula	Mineral Name
39	$MnSeO_3$	
40	$Zn(OH)_2$	
41	ZnO	
42	$ZnCO_3$	
43	$Zn_3(PO_4)_2(4H_2O)$	
44	ZnS	
45	$CaSiO_4$	
46	Hg_2CO_3	
47	$Fe(PO_4)(2H_2O)$	
48	Hg_2HPO_4	
49	Hg_2SO_4	
50	Hg_2Cl_2	
51	$FeOOH$	
52	$Fe(OH)_3$	
53	Fe_2O_3	
54	$CoCO_3$	
55	$Co(OH)_2$	
56	$Co_3(PO_4)_2$	
57	CoS	
58	$Al(OH)_3$	Gibbsite
59	$Al(OH)_3$	Amorphous
60	$AlPO_4$	
61	$AlH_2PO_4(OH)_2$	
62	MgF_2	
63	CaF_2	

2.2.3 Specifying input values

The input file contains all data required to specify the system to be analysed. Data is read from the file by position, so the user, in editting the data, should not re-arrange the file. Certain features are present in the file to aid in this. In the first half of the file, most data values begin in column 25. In the latter portion of the file, headings and titles are provided in order to remind the user where data must reside. In a few cases, the '>' and '<' symbols are used to mark the locations of fields. In order to avoid moving data fields, it is recommended that the input file be editted in overstrike mode. It is also recommended that a backup copy of the original file be kept in case the working copy is damaged beyond repair.

The only instance where records may be deleted or rearranged is in the specification of anions and metals (Table 1). These records are recognized by the program by the combination of an 'A' or 'M' in column one, together with the code number in columns 25-26. (Note that the species name is not read by the program, but appears for the user's information only).

3.0 REPORTING

The following reports may be produced by specifying the report options discussed earlier. All reports are written out to text files which may be viewed through an editor or copied to a printer. The first three types of reports (if requested) are combined into one file, the name of which is created by combining the entries in the "FILENAME" and "ID" fields specified in the input file (Table 1). The main output file is formatted to a width of 132 columns and contains control codes for form feed. This must be taken into account when the file is printed or viewed.

1) Model Parameters and Options Report:
This report is always generated by the program and it lists the various parameters and options that are used to define the current aquatic system.

2) Equilibrium Constants/Activity Coefficients Report:
This report lists the numerical values of the equilibrium constants "K", "ALPHA" values (i.e., the ratio of activity coefficients as they appear in the chemical equilibrium equation), "GAMMA" values (i.e., the activity coefficients) and C values (see section 5.0) used by the program to compute the concentrations involved in the chemical equilibria. This report also includes the solids table which lists the code number recognized by the program for all solids, and the names and formulas of the solids. This report is generated when the "DEFINITIONS" value is set to true (Table 1).

3) Species Report:
A species report lists the concentrations at each pH increment of all the calculated species in solution of the particular metal or anion specified in the data input file. The last column in the report lists the calculated total dissolved value for the anion or metal at each pH increment. If the analysis has gone properly, this number should be the same at each pH increment and be nearly identical to the inputted total dissolved concentration, except when the system is open with respect to an anion or metal because of the presence of a solid, or when the system is open with respect to atmospheric CO_2, in which case dissolved inorganic carbon will not remain constant as

a function of pH. When reports are requested in percentage units, the species concentrations are always reported as a percentage of the calculated total dissolved concentration at each pH increment. One report will be generated for each of the units specified. Note that each report may consist of up to three 'pages' in the file.

4) ASCII File Report

The program can output copies of the species reports to data files which can then be read by external plotting routines. The program reads the "FILENAME" field of each anion or metal. If this field and the "FILE ID" field are non-blank, a separate file will be generated for each selected unit. The file name is created by combining the entries from these two fields and adding the extension '.DA' followed by a code number of 1 to 6 to specify the units reported (1-M, 2-logM, 3-%M, 4-mg/L, 5-log(mg/L), 6-%(mg/L)). The file names are created automatically including the extension, from the entries in the respective fields. Note that all plotting files may be suppressed by setting the 'FILE ID' field to blank even if some 'FILENAME' fields are filled.

The plotting file will not be 'paged' as the main data file is, but may be up to 400 characters wide. The file will contain one record listing the column headings for the report (intended to help identify the contents of the file) followed by the data records as listed in the main output file.

4.0 ERROR PROCESSING AND MESSAGES

To keep error processing under complete program control, the program checks for two types of errors: input errors and calculation errors. As records are input the program checks for errors, and issues messages to indicate where and why records are invalid. When an error is detected, an error report is produced listing the invalid records along with the appropriate error messages. Processing of the data set is then aborted.

Although the frequency of calculation errors is much less than that for input errors, a number of checks are nevertheless made. Such checks include ensuring that the roots of quadratic and cubic equations fall within an allowable range (e.g., if a root "x" should lie between "a" and "b") and that the maximum number of iterations is not exceeded in the iterative calculations. Reiteration stops when the last calculated species concentration value differs from the previous iteration only by a ratio of 1×10^{-4} or less, for all calculated species. Included with each error message is a listing of the values of variables which were involved with the error, as well as an indication of where in the program the error occurred. When an error occurs during the calculation of a system at a particular pH value, the program, after signalling the error, aborts further calculations at that pH increment and attempts to continue with the next pH increment in the range.

Calculations are performed in double precision to 16 decimal digits. The smallest and largest numbers calculated are 0.5×10^{-78} and $0.7 \times 10^{+76}$ respectively.

5.0 TEMPERATURE DEPENDENCE OF K's

The familiar van't Hoff equation is used in the program to calculate the equilibrium constants (K) at various temperatures:

$$K = e^{\{C + m/(273.15 + t)\}}$$

$C = 1.688X10^{-3} \bullet \Delta H_r^\circ + 2.302\log_{10}(K_{25})$

$m = -0.5032 \bullet \Delta H_r^\circ$

t = temperature in degrees Celsius

ΔH_r° = calories/mole, the standard enthalpy change for the reaction.

The expression is valid for the approximate temperature range from 0 to 30°C, and is based on the assumption that the standard enthalpy of the reaction is constant within this temperature range. Whenever sufficient information is not available (i.e., m = 0) to calculate K(t), the equilibrium constant for 25°C is used regardless of the temperature specified. Equilibrium constants which are presently calculable as a function of temperature are marked by an asterisk in the "DEFINITIONS" table (i.e., table of K-values).

6.0 TEMPERATURE DEPENDENCE OF γ's.

Activity coefficients (γ's) were calculated from ionic strength (I) with the Bjernum equation (valid up to approximately I = 0.1 M):

$$\log_{10}\gamma_i = z_i^2 A \frac{\sqrt{I}}{1 + a_i B\sqrt{I}}$$

z_i and a_i are the charge and ionic radius respectively of ion "i".

$A = (0.4875)\ 10^{0.001783 \bullet t}$

$B = (0.3239)\ 10^{0.0005933 \bullet t}$

"t" is the temperature (°C).

A and B were obtained as a function of temperature by curve-fitting published A, B vs temperature-data (Manov et al. 1943).

7.0 IONIC STRENGTH FROM CONDUCTIVITY

The following expression is used in the program to calculate the ionic strength from conductivity:

Ionic strength = Conductivity * $1.8 * 10^{-5}$

Ionic strength is expressed in moles/L and conductivity in mSiemens/cm. The expression is valid in the ionic strength range of 0 - 0.2 moles/L, i. e. for fresh waters. The constant in the above equation was obtained by curve-fitting of published data of ionic strength vs conductivity (Ponnamperuma et al. 1966).

8.0 PROGRAM INFORMATION

The following is the control structure of the routines. It shows the routines controlled by each routine.

MAINLINE
- INITCM
- INPUT
  - WPARMS
- ALPHAC
- INSPEC
- NWMTLS
- NWANIN
- SPCALC
- OUTPUT
  - WDEFNS
  - Wxxx
    - WHEAD
    - WFOOT

Note: Wxxx refers to output routines which are specific to each species (e.g., WSO4 , WFEIII).

8.1 NARRATIVE ON FUNCTION OF ROUTINES

INITCM - Initializes C and M values to calculate K constants.

INPUT - Inputs, syntax checks and decodes a set of parameters.

WPARMS - Writes the input parameters report to output file.

ALPHAC -Computes "ALPHA" values for the current set of parameters.

INSPEC - Initializes the species table and various other values which are dependent upon pH.

NWMTLS - Calculates new concentrations for metals upon each iteration.

NWANIN - Calculates new concentration for anions upon each iteration.

SPCALC - Calculates concentrations of all species and total dissolved concentrations in system when equilibrium is reached.

OUTPUT - Calls all output report routines that were requested by the input parameters.

SETDAT - Library routine which assigns current date.

WDEFNS - Writes the constants definition tables to output file.

Wxxx - Writes aqueous xxx species report.

WHEAD - Writes a header at the top of each new page.

WFOOT - Writes a footer and notes at the bottom of each page.

8.2 INPUT REQUIREMENTS OF ROUTINES

INITCM - None.
INPUT - Data file with input parameters.

WPARMS - All input and default parameters.

ALPHAC - GAMMA values.

INSPEC - pH, "pCO_2 controls TDIC" flag, pCO_2 value, and K/ALPHA ratios.

NWMTLS - Specified metal solids, K/ALPHA ratios.

NWANIN - Specified anion solids, "pCO_2 controls TDIC" flag, and K/ALPHA ratios.

SPCALC - pH, K/ALPHA ratios, anion and metal concentrations and number of pH points for which the system has been successfully evaluated.

OUTPUT - Report flags, K, ALPHA,

GAMMA - species concentrations, anion and metal conversion tables, calculated total dissolved anions and metals, and the pH points successfully evaluated.

SETDAT - None.

WDEFNS - K, ALPHA, GAMMA values.

Wxxx - Number of pH points successfully evaluated, pH values evaluated, equilibrium and total dissolved concentrations of species, and conversion factors as well as calculated total dissolved xxx.

WHEAD - The date, current page number and input title.

WFOOT - The date and current page number.

8.3 PROCESSING

The algorithm solves (positive root) reiteratively polynomial equations for each free anion and metal ion in the system and then uses these to calculate the various species. The coefficients of the polynomial are comprised of the products and ratios of the equilibrium constants of all the species that contain the anion or metal in question. The variable in the polynomial is the concentration of the free anion or metal. The constant part of the equation is the inputted total dissolved concentration of the anion or metal. For example, the carbonate ion concentration would be obtained from the mass balance equation for total dissolved inorganic carbon (TDIC):

$$TDIC=(1+\Sigma L_i)[CO_3]+2(\Sigma Q_i)[CO_3]^2+...$$

The coefficient of the quadratic term of this polynomial is:

$$\Sigma Q_i=\Sigma\frac{K_i}{\alpha_i}M_i$$

M_i is any metal ion involved in the formation of metal-dicarbonate species, K_i is the corresponding equilibrium constant, and α_i is comprised of the products and ratios of the activity coefficients of the ions involved in such a complex. The coefficient of the linear term $\sum L_i$ is similarly defined as $\sum Q_i$, except it involves only mono-carbonate species. The summation in the quadratic term extends over all di-carbonate complexes, and in the linear term over all mono-carbonate complexes. Thus, the equilibrium constants, activity coefficients and either an anion or metal ion of the mono-, di-, and tri-nuclear species make up the coefficients of the linear, quadratic and cubic terms respectively of the polynomial and these are stored in the SPSUM array (APPENDIX III). Similar polynomials represent the mass balance for each metal and anion. For example, the cupric ion concentration would be calculated from the total dissolved copper mass balance equation:

$$TDCu=(1+\Sigma l_i)[Cu]+2(\Sigma q_i)[Cu]^2+...$$

The coefficient of the quadratic term is:

$$\Sigma q_i=\Sigma\frac{K_i}{\alpha_i}A_i$$

The summation ranges over all di-nuclear copper complexex. A_i is any anion involved in such a complex. The coefficient of the linear term is similarly defined except that the summation includes only mono-nuclear complexes of copper.

The processing begins by calculating the coefficients of the metal equations, as described above, and solving the metal equation for the free metal concentrations. The initial metal ion concentration estimate is obtained from the metal mass balance polynomials containing initially only known anion concentrations defined by the pH i.e. hydroxide ion, and in the case of a system open to the atmosphere, carbonate ion. Once the initial free metal ion concentration

estimates have been calculated, the coefficients of the anion equations are calculated, and the free anion concentrations are estimated. These in turn are used to calculate new, more accurate free metal ion concentrations. This iteration process continues between the anion and metal ion polynomials (see APPENDIX III) until the free metal concentrations change by less than 0.01 %. Each chemical species concentration is then simply calculated using the appropriate equilibrium constant, activity coefficients and the free ion concentrations. For example, the concentration of the species $CuCO_3$ and $Cu(CO_3)_2$ would then be calculated as shown:

$[CuCO_3] = [Cu]*Ka(18)*[CO_3]$, and

$[Cu(CO_3)_2] = [Cu]*Ka(19)*[CO_3]^2$;

where Ka(18) and Ka(19) are the respective equilibrium constant for these species (with the activity coefficients incorporated) and the quantities in square brackets are the corresponding free ion concentrations. The numbers in parentheses following Ka are the indices for the equilibrium constants as defined within the program. Species containing hydrogen or hydroxide ions are incorporated into the "constant", e.g. $[CuHCO_3] = [Cu]*k*[CO_3]$ where $k = Ka(27)*[H^+]$.

The total dissolved concentrations are constants in the polynomial and are stored in the arrays "A" and "MTL". Total anion concentrations are stored in the array "A" while total metal concentrations are stored in "MTL".

The variables (i.e., free anion and metal concentrations) are stored in the arrays "XANIN" and "XMTL", respectively.

The various coefficients of the terms in the polynomial are stored in the arrays "SPSUM", "HSP", and "HSPQ". The constants for calculating the species in which there is an anion and metal, are stored in "SPSUM". The first row of "SPSUM" is reserved for storing the constants for calculating the species which contain only metals and hydroxide. The constants for calculating the species which are determined by multiplying an anion by a constant only (where the only cation is hydrogen ion) are stored in the arrays "HSP" and "HSPQ". The species comprised of only 1 of the anion of interest are in "HSP" and those comprised of 2 of the anion of interest are in "HSPQ".

8.4 OUTPUT OF ROUTINES

ALPHAC - ALPHA values.

INITCM - Initialized C and m values for calculation of K values.

INPUT - Parameter report, and/or error messages.

INSPEC - Species table, initialized iteration counter and equilibrium flag, bomb flag, and inorganic carbon concentration if Pco_2 is specified.

NWANIN - Anion concentration and/or errors.

NWMTLS - New metal concentrations and/or errors, and previous metal concentrations.

OUTPUT - Requested reports.

SETDAT - Date in character form.

SPCALC - Species concentrations to be output, calculated total dissolved values, and the current number of pH points successfully evaluated.

WDEFNS - Definitions report.

WFOOT - Footer and notes at bottom of the current page of output.

WHEAD - Header at top of new page of output.

WPARMS - Input parameters report.

Wxxx - A species report of all species containing xxx.

9.0 EQUATION COEFFICIENT SIGNIFICANCE TESTS

Tests were introduced to the program to determine the significance of the coefficients used in solving a polynomial, since some terms in the calculation of the roots of the quadratic and cubic could become insignificant in relation to others. The tests eliminate insignificant coefficients, simplify the equation, (i.e., a cubic could become a quadratic equation and a quadratic could become a linear equation) and produce a more accurate solution.

9.1 QUADRATIC COEFFICIENT TEST

An exact solution of the quadratic equation provides the free ion concentration in question.

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

However, when b^2 becomes insignificant compared to 4ac in the equation then the computer cannot solve the equation. Similarly, when 4ac is insignificant compared to b^2, a computational problem arises in:

$$\frac{b^2}{4ac} > 10^{10}$$

An upper limit of 10^{10} on the size of the ratio was put in place; the term "4ac" is considered negligibly small and discarded if this ratio is exceeded. 10^{10} is used because the calculations are done to 14 significant digits, and at least 4 significant figures in the calculations are then assured.

9.2 CUBIC COEFFICIENT TEST

The solution to the cubic equation:

$$ax^3 + bx^2 + cx + d = 0$$

is obtained by a method of successive approximations. Starting with -d/c as an estimate of the root, the program performs 100 iterations of adding or subtracting a small correction to the root. The initial correction is -d/2c and is divided by 2 on each iteration. The process is stopped when the root becomes consistent to one part in 10,000 (i.e., 0.01%).

10.0 PROGRAM UPDATING

The program was designed to be expandable in terms of adding new anions and metals, new species of existing anions and metals, and new solids to the system. Such upgrading requires a text editor and a FORTRAN compiler compatible with the source code. The following sections describe the places in the program where changes must be made to accomodate additional ions.

10.1 ADDING AN ANION OR METAL TO THE SYSTEM

1. Assign the species an "A" number if it is an anion and or "M" number if it is metal. If there is no more room in the "A" or "MTL" array, increment its size and assign the variable "NAVALS" or "NMVALS" the new size. If the "A" array is incremented then increase the number of rows of "SPSUM" to this size. Also increase the arrays "HSP" and "HSP2" to this size. If the "MTL" array is incremented then increase the number of columns of "SPSUM" to this size. (Mainline of program)

2. Place the equation to calculate the constants of the mass balance equation in the array "SPSUM" (3-dimensional array, see Appendix III). The first dimension is indexed by the anion, the second dimension is indexed by the metal, and the third is indexed by the exponents of the anion and metal concentrations in the mass balance equation. If the species contains:

1 of the metal and 1 of the anion, use index 1

1 of the metal and 2 of the anion, use index 2

1 of the metal and 3 of the anion, use index 3

2 of the metal and 1 of the anion, use index 4

2 of the metal and 2 of the anion, use index 5

2 of the metal and 3 of the anion, use index 6

3 of the metal and 1 of the anion, use index 7

3 of the metal and 2 of the anion, use index 8

3 of the metal and 3 of the anion, use index 9

As an example, the equation for the species FeHEDTA, containing one ion of anion 3 and one ion of metal 4 (the [H] is determined by pH and is calculated into the constant), would be entered into SPSUM (3,4,1). The equation for the species $(FeHEDTA)_2$, containing two ions of anion 3 and two of metal 4, would be entered into SPSUM(3,4,5). A pictorial presentation of the SPSUM array is given in APPENDIX III.

When two species have the same index into SPSUM (e.g. CuCO3 and CuHCO3), the entry should be the sum of the equations for the two species.

The species with only an anion and hydrogen ion are stored in"HSP" if the anion is a linear term and in "HSPQ" if the anion is a quadratic term. No species containing only hydrogen and a cubic term are included in the program's analysis.

For the purposes of discussion here, hydroxide ion is considered anion 1 (even though its concentration is calculated instead of being entered), so no special arrays are used for this anion. (INSPEC subroutine)

3. The conversion factor for the ion (mg/mole) will have to be added to "CONVTA" (anion) or "CONVTM" (metal). The sizes of these arrays must be increased as necessary. (Mainline)

4. The new species can then be added to the output routines of existing anions and metals as described in section 10.4.

5. The new species report for the new anions and metals can also be added to the system as described in section 10.5.

6. If there are any new solids, they can be added as described in section 10.2.

7. The "K", "ALPHA" and "GAMMA" values must then be added to the definitions report.

8. Add statements to the INPUT

routine to read and to the WPARMS routine to write the total dissolved concentration of the ion. Modify the MACS80.INPUT file to provide space for the new entry.

10.2 ADDING A SOLID TO THE SYSTEM

1. Increment the size of the arrays "KA", "ALPHA", "C", and "M" and insert the new alpha equation and c and m values required. (ALPHAC, INITCM subroutines).
2. Set the variable "NKVALS" to the size of "KA", which should also be equal to the size of "ALPHA", "C", and "M". (Mainline)
3. The formula for calculating the concentration of the anion from the solid should be placed in the routine "NWANIN". The formula for calculating the concentration of the metal from the solid should be placed in the routine "NWMTL".

10.3 ADDING AN INPUT PARAMETER

1. Code a read statement in the INPUT subroutine and update the accompanying FORMAT statement. Edit MACS80.INPUT to provide space for entry of the parameter.
2. Code a write statement in the routine "WPARMS" and update the accompanying format statement.
3. Update the appropriate common statements depending on where the parameter is needed. Initialize the parameter in the routine "MAIN".
4. Implement the new parameter in the program.

10.4 ADDING CHEMICAL SPECIES TO OUTPUT ROUTINES

1. Assign the new total number of species to NGVALS and increase the size of SPSUM, X, GAM, Z and A0 to this value. Assign the new total number of activity constants to NKVALS and increase the size of KA, C, M and ALPHA to this value.
2. Assign values to the new entries in C, M, Z and A0. Code the equations to calculate the new ALPHA value in subroutine ALPHAC and the new SPSUM value in subroutine INSPEC.
3. The species concentration should be calculated at each pH in the routine "SPCALC" and placed in the array "X" indexed by the species number.
4. The species concentrations stored in array "X" should be placed in the appropriate output routines "Wxxx" (i.e. the metal and anion output routines). The appropriate format statements should also be updated to print the chemical formula for the species.
5. If the species is an organic carbon species being placed in the organic carbon output routine, "WOC" then it should be divided by another conversion factor. The factor is 3.36×10^2 if there is an A and 6.72×10^2 if there is an A_2.

10.5 ADDING A CHEMICAL REPORT TO THE SYSTEM

1. Create an output routine called "Wxxx", where xxx is the chemical formula of the new chemical (e.g., SO_4, Cl, NH_3, Cu). Write the routine with the same structure as the other output routines "Wxxx".
2. The species that will be printed out will be the new species added in section 10.4.
3. Place a call to this new routine in the "OUTPUT" routine, in the case structure for anions or the case structure for

metals, depending on whether the new species is an anion or metal.

11.0 REFERENCES

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APPENDIX I

Parameters and Options: Format of Input File
All records have one field in common, the command field. The command field starts in column 1, ends in column 24, and contains character data.

Line	Field Name	Starting Position	Length	Data Type
1	TITLE	25	48	character
2	Temperature	25	10	numeric
3	Pco2	25	10	numeric
	CONTROLS TDIC	53	1	logical
4	Ionic Strength	25	10	numeric
5	Conductivity	25	10	numeric
6	pH Range MAX	25	6	numeric
	MIN	36	6	numeric
	INC	47	6	numeric
7	pH Specific	25	6	numeric
Output Units				
9	Moles/l	25	1	logical
	Mg/l	32	1	logical

APPENDIX I (continued)

Parameters and Options: Format of Input File (Output Units) Cont'd

Line	Field Name	Starting Position	Length	Data Type
10	Log(moles/l)	25	1	logical
	Log(mg/l)	32	1	logical
11	%(moles/l)	25	1	logical
	%(mg/l)	32	1	logical
12	Definitions	25	1	logical
13	Output file	18	4	character
	Output file ID	33	4	character
14-end	Species type	1	1	character
	Species number	25	2	numeric
	Concentration	30	10	numeric
	Units	45	2	character
	Solid number	50	2	numeric
	Species report	60	1	logical
	Data file name	66	4	character

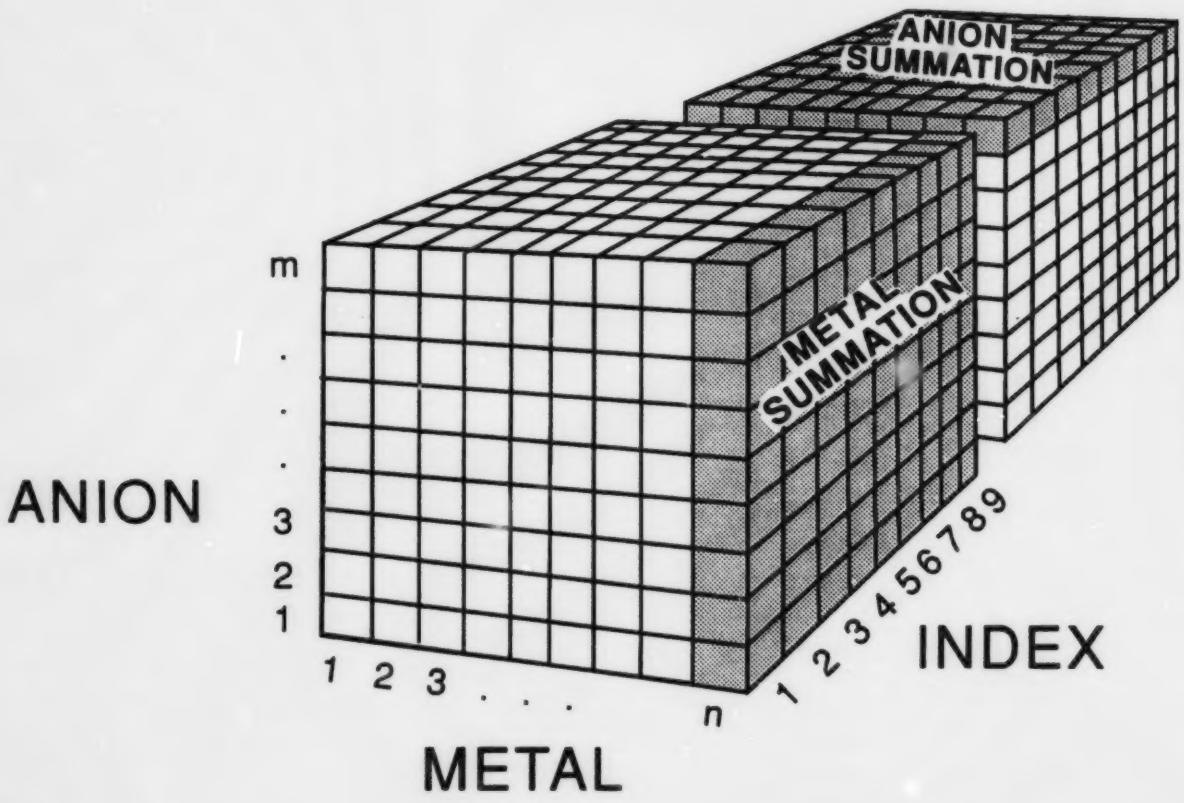
Note: The titles under "field name" are only a description of the fields.

APPENDIX II

Listing of Anions and Metals

Anion	Name	Metal	Name
1	Hydroxide	1	Sodium
2	Sulfate	2	Magnesium
3	EDTA	3	Calcium
4	NTA	4	Iron (III)
5	Inorganic carbon	5	Mercury (I)
6	Chloride	6	Mercury (II)
7	Organic carbon	7	Cadmium
8	Selenite	8	Copper
9	Silicate	9	Iron (II)
10	Ammonia	10	Manganese
11	Ortho-phosphate	11	Zinc
12	Acetate	12	Potassium
13	Sulfide	13	Cobalt
14	Suspended sediment	14	Aluminum
15	Flouride		

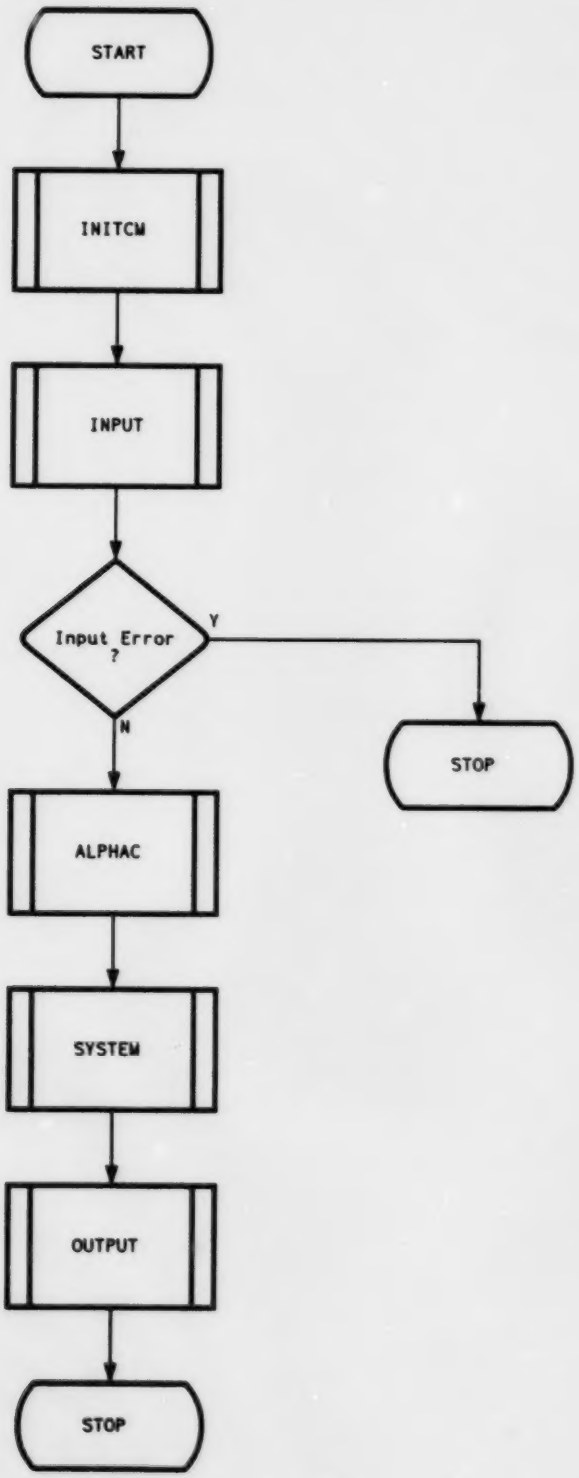
APPENDIX III: Illustration of SPSUM Array



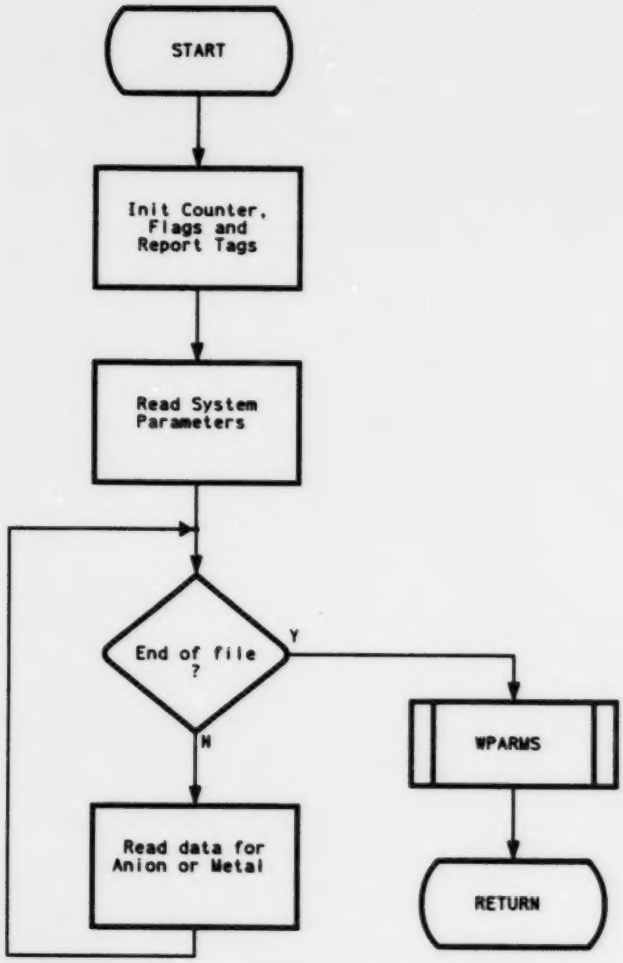
APPENDIX IV

System Flowcharts

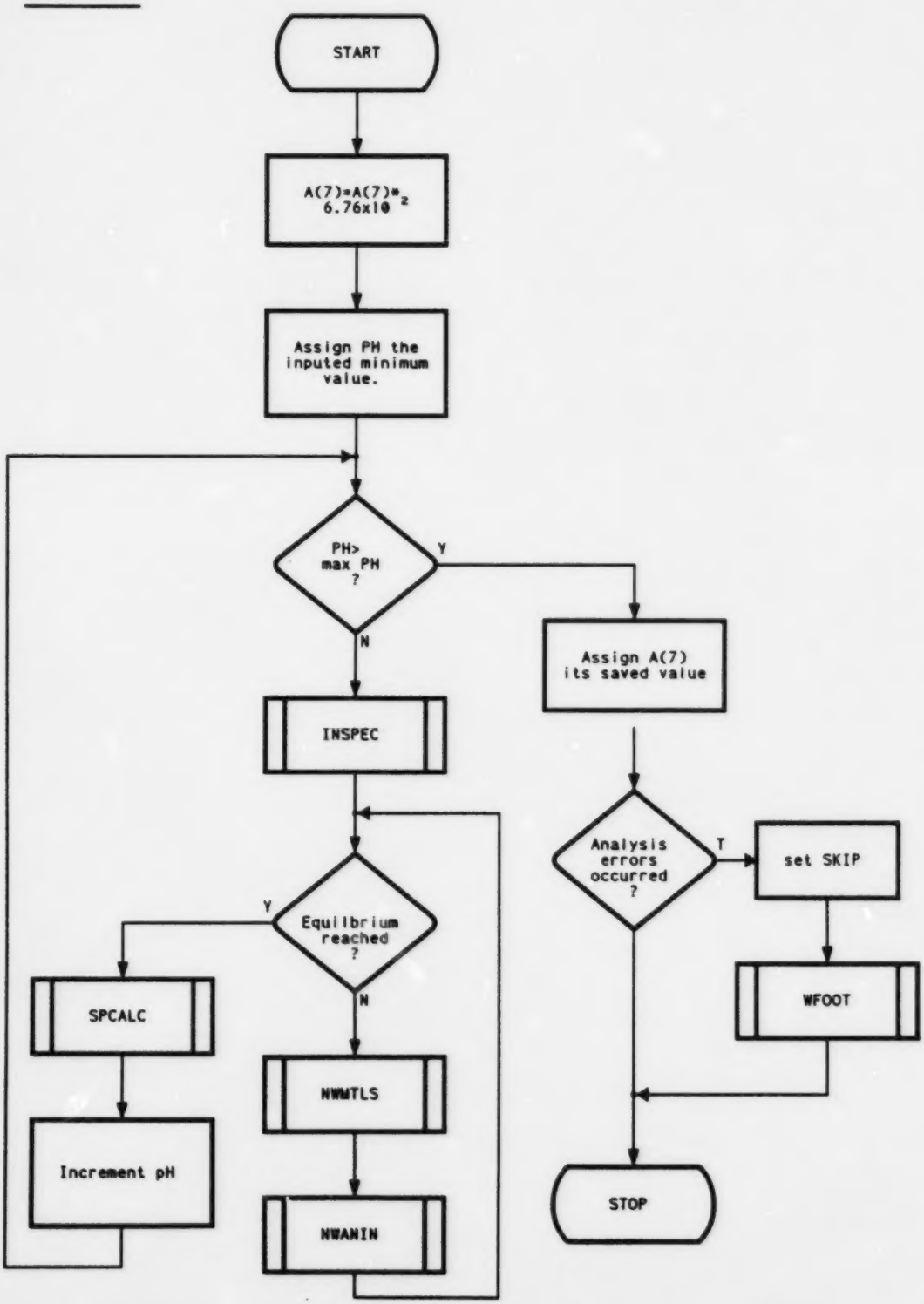
MAINLINE


START
INITCM
INPUT
Input Error ?
Y
N
STOP
ALPHAC
SYSTEM
OUTPUT
STOP

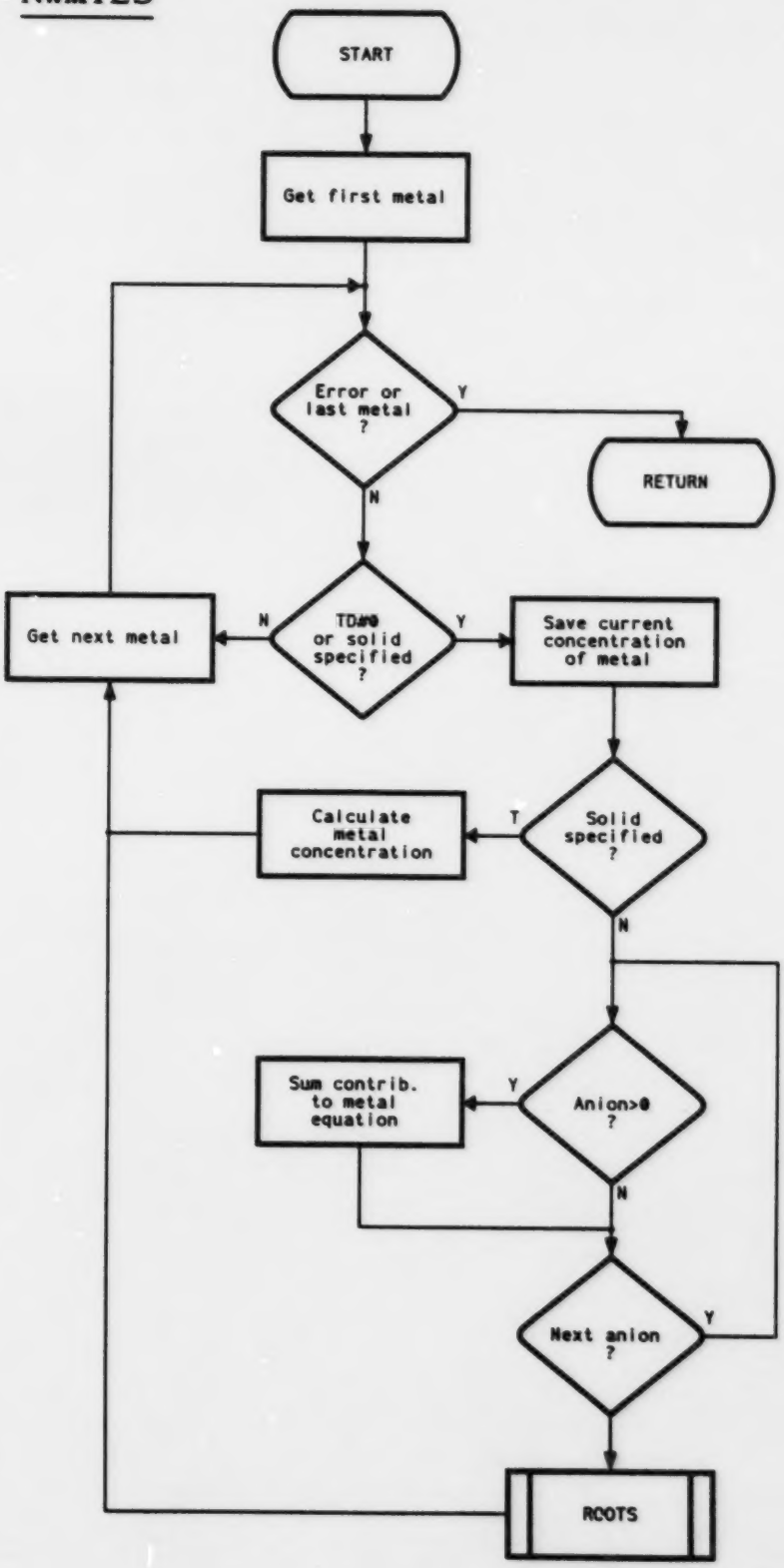
INPUT


START
Init Counter, Flags and Report Tags
Read System Parameters
End of file ?
Y
N
WPARMS
Read data for Anion or Metal
RETURN

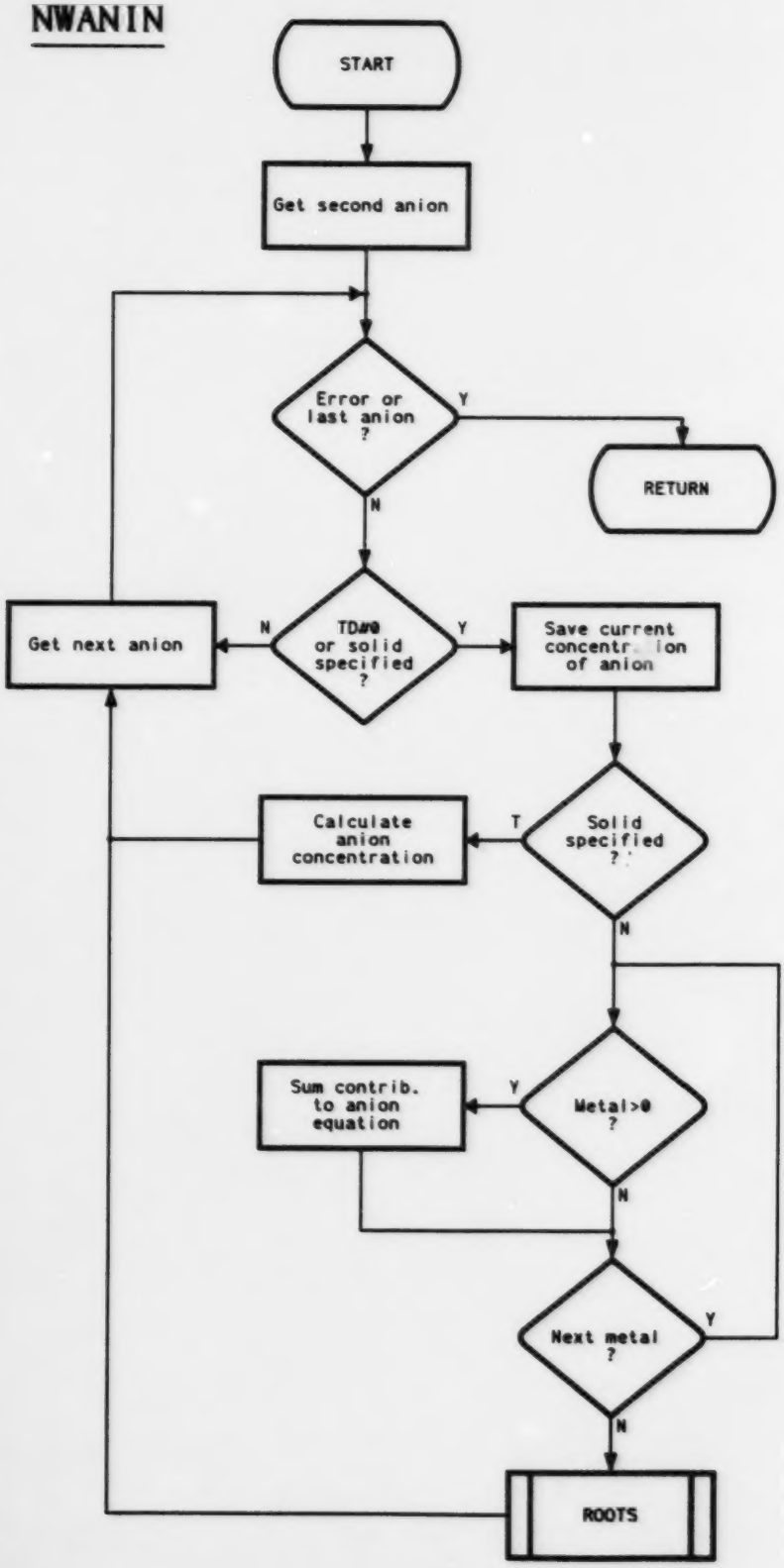
SYSTEM


START
A(7)=A(7)*
6.76x10 -2
Assign PH the inputed minimum value.
PH> max PH ?
Y
N
Assign A(7) its saved value
INSPEC
Analysis errors occurred ?
T
set SKIP
Y
Equilbrium reached ?
N
WFOOT
SPCALC
NWMTLS
Increment pH
NWANIN
STOP

NWMTLS

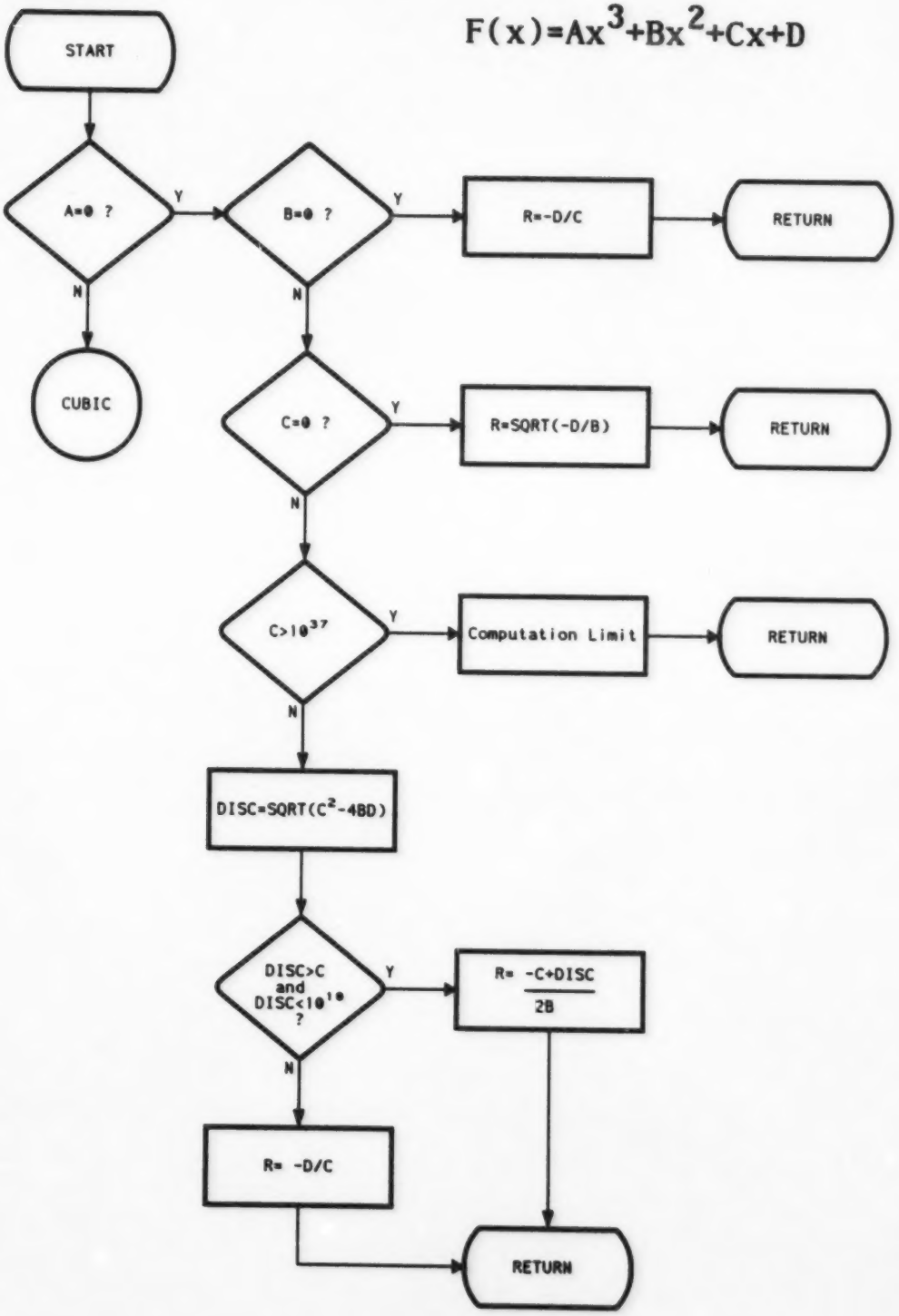

START
Get first metal
Error or last metal ?
Y
RETURN
N
TD#0 or solid specified ?
N
Y
Get next metal
Save current concentration of metal
Calculate metal concentration
T
Solid specified ?
N
Sum contrib. to metal equation
Y
Anion>0 ?
N
Next anion ?
Y
ROOTS

NWANIN


START
Get second anion
Error or last anion ?
Y
RETURN
N
TD#0 or solid specified ?
N
Y
Get next anion
Save current concentration of anion
Calculate anion concentration
T
Solid specified ?
N
Sum contrib. to anion equation
Y
Metal>0 ?
N
Next metal ?
Y
N
ROOTS

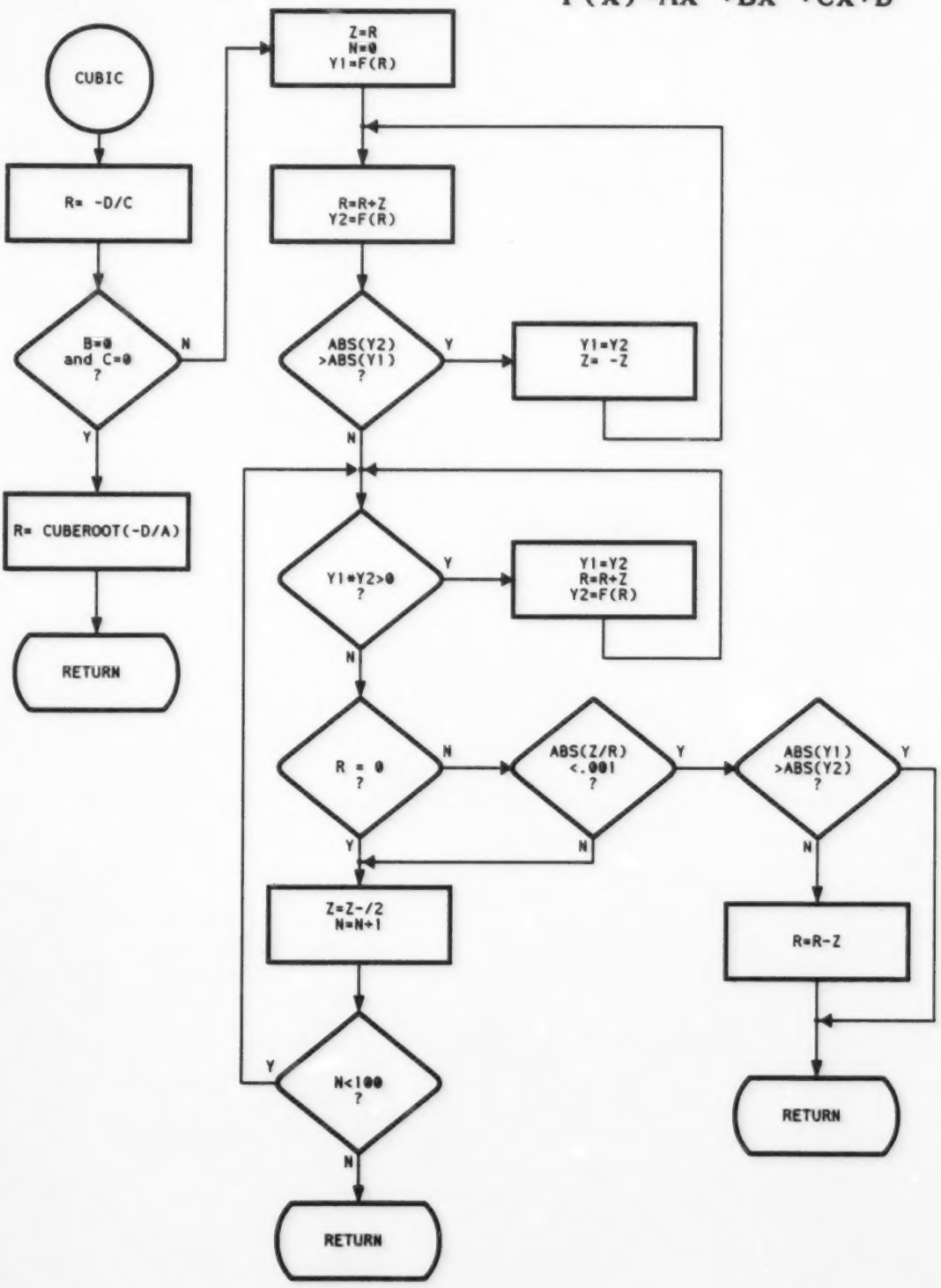
ROOTS

$$F(x)=Ax^3+Bx^2+Cx+D$$

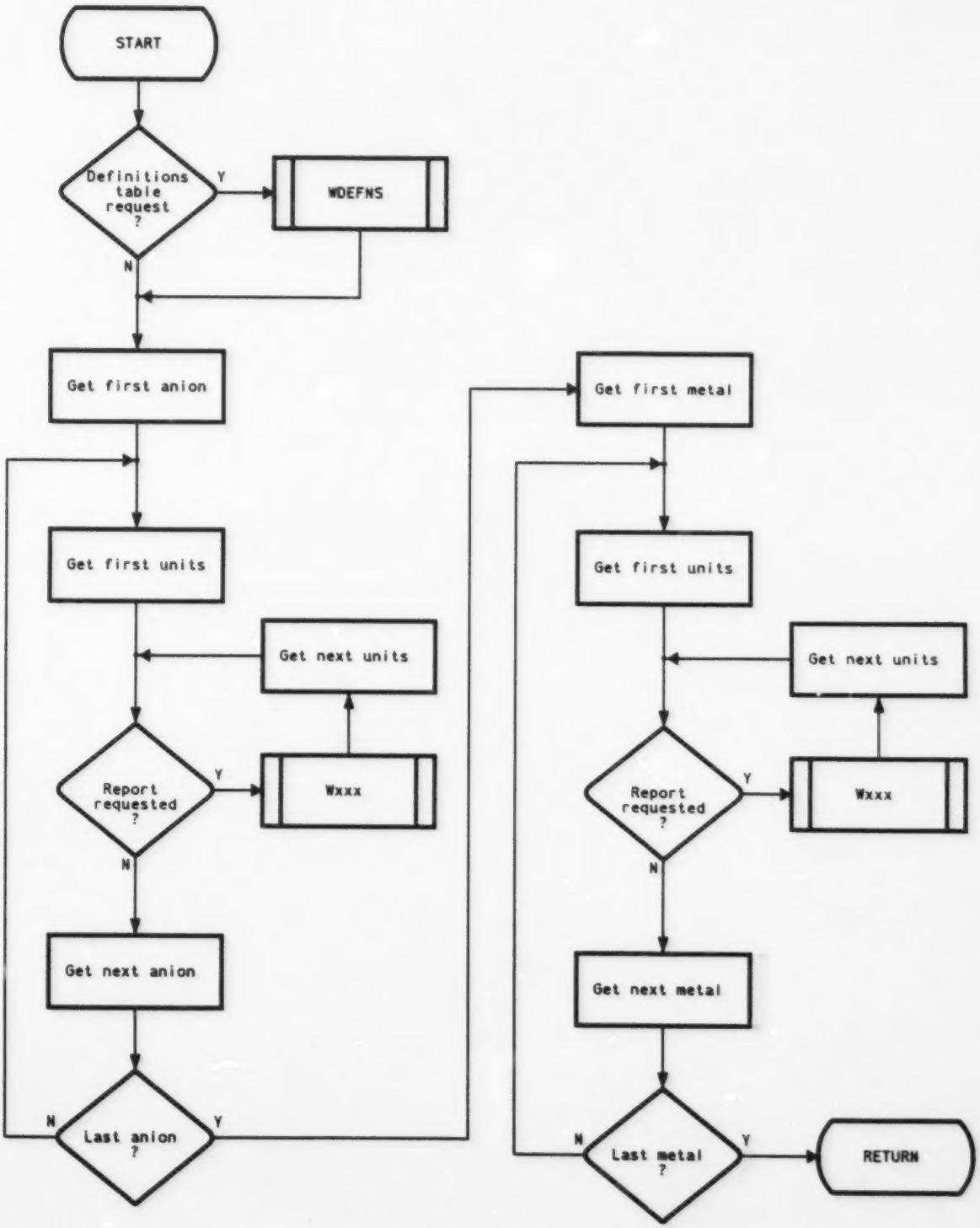


ROOTS (cont)

$$F(x)=Ax^3+Bx^2+Cx+D$$



OUTPUT


START
Definitions table request ?
Y
N
WDEFNS
Get first anion
Get first units
Get next units
Report requested ?
Y
N
Wxxx
Get next anion
Last anion ?
N
Y
Get first metal
Get first units
Get next units
Report requested ?
Y
N
Wxxx
Get next metal
Last metal ?
N
Y
RETURN

APPENDIX V

Sample Run of MACS80 Output

11/12/1991

DEPARTMENT OF FISHERIES & OCEANS - WESTERN REGION

CHEMICAL METHODOLOGY - R. WAGEMANN

STANDARD RIVER WATER TEST DATA

TEMPERATURE ..... 25.000000 DEG C
PCO2 ..... .000350 ATM. CONTROLS T.D. IC = F

IONIC STRENGTH .... .003600 MOLES/L
CONDUCTIVITY .... .000000 UMHOS/CM

pH RANGE:
MINIMUM ..... 5.00 MAXIMUM ..... 7.50 INCREMENT ..... .20

pH SPECIFIC 8.01

SEDIMENT CD CONSTANT .5435150D-04 *10**(.5064000*PH)

OUTPUT OPTIONS:

UNITS:
MG/L

TABLES:
DEFINITIONS ... F

OUTPUT FILE: MACSRUN0.DAT

NOTE : 'T.D.' MEANS TOTAL DISSOLVED.
NOTE : ALL MOLES/L AND MG/L VALUES ARE CONCENTRATIONS AS OPPOSED TO ACTIVITIES.
NOTE : A CONCENTRATION OF 0 CAN MEAN EITHER THE T.D. CONCENTRATION WAS 0 OR THE SPECIES CONCENTRATION WAS APPROACHING 0.

11/12/1991

DEPARTMENT OF FISHERIES & OCEANS - WESTERN REGION
CHEMICAL METHODOLOGY - R. WAGEMANN

STANDARD RIVER WATER TEST DATA

TOTAL DISSOLVED VALUES:

	MOLES/L	MG/L	SOLID NUMBER	SPECIES REPORT	ASCII FILE NAME
SULFATE	8.01522D-05	2.57000D+00	00	F	
EDTA	0.00000D+00	0.00000D+00	00	F	
NTA	0.00000D+00	0.00000D+00	00	F	
INORGANIC CARBON	1.23220D-03	1.48000D+01	00	T	ICRUN0
CHLORIDE	2.79243D-04	9.90000D+00	00	F	
ORGANIC CARBON	2.08143D-04	2.50000D+00	00	F	
SELENITE	2.53293D-09	2.00000D-04	00	F	
SILICATE	3.03354D-04	8.52000D+00	00	F	
AMMONIA	7.99600D-06	1.12000D-01	00	F	
ORTHO-PHOSPHATE	6.77988D-06	2.10000D-01	00	F	
ACETATE	0.00000D+00	0.00000D+00	00	F	
SULFIDE	6.23752D-08	2.00000D-03	00	F	
SEDIMENT	2.00000D+00	2.00000D+00	00	F	
FLUORIDE	0.00000D+00	0.00000D+00	00	F	
SODIUM	5.21966D-04	1.20000D+01	00	F	
MAGNESIUM	3.08490D-04	7.50000D+00	00	F	
CALCIUM	3.04391D-04	1.22000D+01	00	F	
IRON(III)	1.25342D-07	7.00000D-03	00	F	
MERCURY(I)	0.00000D+00	0.00000D+00	00	F	
MERCURY(II)	4.98529D-11	1.00000D-05	00	F	
CADMIUM	8.89680D-10	1.00000D-04	00	F	
COPPER	7.86906D-09	5.00000D-04	00	T	CURUN0
IRON(II)	2.68591D-07	1.50000D-02	00	F	
MANGANESE(II)	8.00903D-08	4.40000D-03	00	F	
ZINC	7.49465D-09	4.90000D-04	00	F	
POTASSIUM	3.58075D-05	1.40000D+00	00	F	
COBALT	0.00000D+00	0.00000D+00	00	F	
ALUMINUM	7.41235D-07	2.00000D-02	00	F	

NOTE : 'T.D.' MEANS TOTAL DISSOLVED.
NOTE : ALL MOLES/L AND MG/L VALUES ARE CONCENTRATIONS AS OPPOSED TO ACTIVITIES.
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11/12/1991

DEPARTMENT OF FISHERIES & OCEANS - WESTERN REGION

CHEMICAL METHODOLOGY - R. WAGEMANN

STANDARD RIVER WATER TEST DATA

INORGANIC CARBON SYSTEM IN MG/L IN TERMS OF CARBON

SOLID =

pH	CO3(-2)	HCO3(-)	H2CO3(0)	MgCO3(0)	MgHCO3(+)	CaCO3(0)	CaHCO3(+)	CuCO3(0)	CuHCO3(+)	Cu(CO3)2(-2)
5.00	3.9166D-06	6.8311D-01	1.4097D+01	5.4933D-07	1.3678D-03	9.9786D-07	1.6019D-03	9.7840D-08	3.8594D-07	1.2128D-13
5.20	9.5840D-06	1.0547D+00	1.3733D+01	1.3439D-06	2.1114D-03	2.4412D-06	2.4727D-03	2.3798D-07	5.9230D-07	7.2187D-13
5.40	2.3122D-05	1.6055D+00	1.3190D+01	3.2412D-06	3.2129D-03	5.8873D-06	3.7626D-03	5.6791D-07	8.9184D-07	4.1560D-12
5.60	5.4591D-05	2.3917D+00	1.2398D+01	7.6492D-06	4.7841D-03	1.3893D-05	5.6023D-03	1.3144D-06	1.3024D-06	2.2710D-11
5.80	1.2524D-04	3.4620D+00	1.1323D+01	1.7537D-05	6.9205D-03	3.1849D-05	8.1034D-03	2.9069D-06	1.8173D-06	1.1522D-10
6.00	2.7658D-04	4.8239D+00	9.9547D+00	3.8697D-05	9.6352D-03	7.0269D-05	1.1281D-02	6.0074D-06	2.3697D-06	5.2586D-10
6.20	5.8307D-04	6.4166D+00	8.3548D+00	8.1499D-05	1.2804D-02	1.4797D-04	1.4989D-02	1.1283D-05	2.8083D-06	2.0822D-09
6.40	1.1672D-03	8.1048D+00	6.6584D+00	1.6297D-04	1.6155D-02	2.9586D-04	1.8909D-02	1.8715D-05	2.9390D-06	6.9139D-09
6.60	2.2181D-03	9.7176D+00	5.0372D+00	3.0935D-04	1.9348D-02	5.6153D-04	2.2644D-02	2.6835D-05	2.6590D-06	1.8839D-08
6.80	4.0198D-03	1.1112D+01	3.6343D+00	5.6002D-04	2.2100D-02	1.0165D-03	2.5863D-02	3.3049D-05	2.0662D-05	4.2048D-08
7.00	7.0042D-03	1.2216D+01	2.5210D+00	9.7481D-04	2.4272D-02	1.7692D-03	2.8402D-02	3.5253D-05	1.3906D-06	7.8149D-08
7.20	1.1841D-02	1.3031D+01	1.6967D+00	1.6464D-03	2.5865D-02	2.9877D-03	3.0263D-02	3.3138D-05	8.2477D-07	1.2419D-07
7.40	1.9582D-02	1.3597D+01	1.1171D+00	2.7204D-03	2.6965D-02	4.9356D-03	3.1544D-02	2.8024D-05	4.4008D-07	1.7369D-07
8.01	8.4090D-02	1.4333D+01	2.8904D-01	1.1639D-02	2.8321D-02	2.1078D-02	3.3068D-02	1.0774D-05	4.1533D-08	2.8675D-07

NOTE : 'T.D.' MEANS TOTAL DISSOLVED.

NOTE : ALL MOLES/L AND MG/L VALUES ARE CONCENTRATIONS AS OPPOSED TO ACTIVITIES.

NOTE : A CONCENTRATION OF 0 CAN MEAN EITHER THE T.D. CONCENTRATION WAS 0 OR THE SPECIES CONCENTRATION WAS APPROACHING 0.

DEPARTMENT OF FISHERIES & OCEANS - WESTERN REGION

CHEMICAL METHODOLOGY - R. WAGEMANN

STANDARD RIVER WATER TEST DATA

INORGANIC CARBON SYSTEM IN MG/L IN TERMS OF CARBON

SOLID =

pH	MnHCO3(+)	AlCO3(+)	T.D.IC
5.00	2.6537D-06	6.4399D-05	1.4783D+01
5.20	4.0912D-06	7.0280D-05	1.4792D+01
5.40	6.2137D-06	6.6529D-05	1.4802D+01
5.60	9.2274D-06	5.5884D-05	1.4800D+01
5.80	1.3300D-05	4.2086D-05	1.4800D+01
6.00	1.8431D-05	2.8478D-05	1.4800D+01
6.20	2.4362D-05	1.7351D-05	1.4800D+01
6.40	3.0567D-05	9.5694D-06	1.4800D+01
6.60	3.6419D-05	4.8201D-06	1.4800D+01
6.80	4.1418D-05	2.2427D-06	1.4800D+01
7.00	4.5337D-05	9.7484D-07	1.4800D+01
7.20	4.8201D-05	3.9921D-07	1.4800D+01
7.40	5.0178D-05	1.5467D-07	1.4800D+01
8.01	5.2664D-05	6.0309D-09	1.4800D+01

NOTE : 'T.D.' MEANS TOTAL DISSOLVED.

NOTE : ALL MOLES/L AND MG/L VALUES ARE CONCENTRATIONS AS OPPOSED TO ACTIVITIES.

NOTE : A CONCENTRATION OF 0 CAN MEAN EITHER THE T.D. CONCENTRATION WAS 0 OR THE SPECIES CONCENTRATION WAS APPROACHING 0.

11/12/1991

DEPARTMENT OF FISHERIES & OCEANS - WESTERN REGION — CHEMICAL METHODOLOGY - R. WAGEMANN

STANDARD RIVER WATER TEST DATA

COPPER SYSTEM IN MG/L IN TERMS OF COPPER

SOLID =

pH	Cu(+2)	CuOH(+)	Cu(OH)2(0)	Cu(OH)3(-)	Cu(OH)4(-2)	Cu2(OH)2(+2)	CuSO4(0)	CuEDTA(-2)	CuHEDTA(-)	CuOHEDTA(-3)
5.00	4.9073D-04	8.2055D-07	7.9649D-08	6.4490D-16	1.2441D-23	1.5833D-12	4.9231D-06	0.0000D+00	0.0000D+00	0.0000D+00
5.20	4.8778D-04	1.2927D-06	1.9887D-07	2.5519D-15	7.8024D-23	3.9293D-12	4.8952D-06	0.0000D+00	0.0000D+00	0.0000D+00
5.40	4.8250D-04	2.0265D-06	4.9412D-07	1.0049D-14	4.8696D-22	9.6574D-12	4.8432D-06	0.0000D+00	0.0000D+00	0.0000D+00
5.60	4.7298D-04	3.1485D-06	1.2167D-06	3.9218D-14	3.0119D-21	2.3310D-11	4.7484D-06	0.0000D+00	0.0000D+00	0.0000D+00
5.80	4.5596D-04	4.8104D-06	2.9462D-06	1.5051D-13	1.8320D-20	5.4415D-11	4.5781D-06	0.0000D+00	0.0000D+00	0.0000D+00
6.00	4.2668D-04	7.1345D-06	6.9253D-06	5.6072D-13	1.0817D-19	1.1969D-10	4.2845D-06	0.0000D+00	0.0000D+00	0.0000D+00
6.20	3.8015D-04	1.0074D-05	1.5498D-05	1.9888D-12	6.0807D-19	2.3865D-10	3.8176D-06	0.0000D+00	0.0000D+00	0.0000D+00
6.40	3.1497D-04	1.3229D-05	3.2256D-05	6.5602D-12	3.1788D-18	4.1153D-10	3.1634D-06	0.0000D+00	0.0000D+00	0.0000D+00
6.60	2.3766D-04	1.5821D-05	6.1136D-05	1.9707D-11	1.5134D-17	5.8857D-10	2.3872D-06	0.0000D+00	0.0000D+00	0.0000D+00
6.80	1.6150D-04	1.7039D-05	1.0436D-04	5.3313D-11	6.4891D-17	6.8271D-10	1.6223D-06	0.0000D+00	0.0000D+00	0.0000D+00
7.00	9.8869D-05	1.6532D-05	1.6047D-04	1.2993D-10	2.5065D-16	6.4267D-10	9.9323D-07	0.0000D+00	0.0000D+00	0.0000D+00
7.20	5.4977D-05	1.4569D-05	2.2414D-04	2.8763D-10	8.7939D-16	4.9915D-10	5.5233D-07	0.0000D+00	0.0000D+00	0.0000D+00
7.40	2.8112D-05	1.1807D-05	2.8789D-04	5.8552D-10	2.8373D-15	3.2784D-10	2.8245D-07	0.0000D+00	0.0000D+00	0.0000D+00
8.01	2.5170D-06	4.3066D-06	4.2777D-04	3.5442D-09	6.9964D-14	4.3613D-11	2.5296D-08	0.0000D+00	0.0000D+00	0.0000D+00

NOTE : 'T.D.' MEANS TOTAL DISSOLVED.

NOTE : ALL MOLES/L AND MG/L VALUES ARE CONCENTRATIONS AS OPPOSED TO ACTIVITIES. NOTE : A CONCENTRATION OF 0 CAN MEAN EITHER THE T.D. CONCENTRATION WAS 0 OR THE SPECIES CONCENTRATION WAS APPROACHING 0.

11/12/1991

DEPARTMENT OF FISHERIES & OCEANS - WESTERN REGION

CHEMICAL METHODOLOGY - R. WAGEMANN

STANDARD RIVER WATER TEST DATA

COPPER SYSTEM IN MG/L IN TERMS OF COPPER

SOLID =

pH	CuNTA(-)	Cu(NTA)2(-4)	CuOHNTA(-2)	CuCO3(0)	Cu(CO3)2(-2)	CuHCO3(+)	CuCl(+)	CuCl2(0)	CuA2	CuNH3(+2)
5.00	0.0000D+00	0.0000D+00	0.0000D+00	5.1759D-07	3.2080D-13	2.0417D-06	2.6697D-07	3.3774D-11	6.1805D-07	2.3345D-09
5.20	0.0000D+00	0.0000D+00	0.0000D+00	1.2589D-06	1.9094D-12	3.1334D-06	2.6536D-07	3.3571D-11	1.1707D-06	3.6775D-09
5.40	0.0000D+00	0.0000D+00	0.0000D+00	3.0044D-06	1.0993D-11	4.7180D-06	2.6249D-07	3.3207D-11	2.1470D-06	5.7651D-09
5.60	0.0000D+00	0.0000D+00	0.0000D+00	6.9534D-06	6.0071D-11	6.8897D-06	2.5731D-07	3.2552D-11	3.8000D-06	8.9560D-09
5.80	0.0000D+00	0.0000D+00	0.0000D+00	1.5378D-05	3.0478D-10	9.6139D-06	2.4805D-07	3.1381D-11	6.4538D-06	1.3682D-08
6.00	0.0000D+00	0.0000D+00	0.0000D+00	3.1780D-05	1.3909D-09	1.2536D-05	2.3212D-07	2.9366D-11	1.0408D-05	2.0288D-08
6.20	0.0000D+00	0.0000D+00	0.0000D+00	5.9690D-05	5.5077D-09	1.4856D-05	2.0681D-07	2.6163D-11	1.5677D-05	2.8638D-08
6.40	0.0000D+00	0.0000D+00	0.0000D+00	9.9006D-05	1.8288D-08	1.5548D-05	1.7135D-07	2.1677D-11	2.1602D-05	3.7588D-08
6.60	0.0000D+00	0.0000D+00	0.0000D+00	1.4196D-04	4.9831D-08	1.4066D-05	1.2929D-07	1.6357D-11	2.6737D-05	4.4917D-08
6.80	0.0000D+00	0.0000D+00	0.0000D+00	1.7484D-04	1.1122D-07	1.0930D-05	8.7861D-08	1.1115D-11	2.9464D-05	4.8316D-08
7.00	0.0000D+00	0.0000D+00	0.0000D+00	1.8649D-04	2.0671D-07	7.3563D-06	5.3787D-08	6.8046D-12	2.8979D-05	4.6786D-08
7.20	0.0000D+00	0.0000D+00	0.0000D+00	1.7531D-04	3.2849D-07	4.3632D-06	2.9909D-08	3.7837D-12	2.5691D-05	4.1104D-08
7.40	0.0000D+00	0.0000D+00	0.0000D+00	1.4825D-04	4.5941D-07	2.3281D-06	1.5294D-08	1.9348D-12	2.0816D-05	3.3149D-08
8.01	0.0000D+00	0.0000D+00	0.0000D+00	5.6997D-05	7.5848D-07	2.1971D-07	1.3693D-09	1.7323D-13	7.3877D-06	1.1617D-08

NOTE : 'T.D.' MEANS TOTAL DISSOLVED.

NOTE : ALL MOLES/L AND MG/L VALUES ARE CONCENTRATIONS AS OPPOSED TO ACTIVITIES.

NOTE : A CONCENTRATION OF 0 CAN MEAN EITHER THE T.D. CONCENTRATION WAS 0 OR THE SPECIES CONCENTRATION WAS APPROACHING 0.

11/12/1991

DEPARTMENT OF FISHERIES & OCEANS - WESTERN REGION

CHEMICAL METHODOLOGY - R. WAGEMANN

STANDARD RIVER WATER TEST DATA

COPPER SYSTEM IN MG/L IN TERMS OF COPPER

SOLID =

pH	Cu(NH3)2(+2)	Cu(NH3)3(+2)	CuAc(+)	CuAc2(0)	SSCu	CuF(+)	T.D.Cu
5.00	2.6660D-15	6.8618D-22	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
5.20	6.6561D-15	2.7151D-21	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
5.40	1.6537D-14	1.0690D-20	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
5.60	4.0712D-14	4.1709D-20	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
5.80	9.8559D-14	1.6001D-19	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
6.00	2.3158D-13	5.9576D-19	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
6.20	5.1794D-13	2.1111D-18	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
6.40	1.0769D-12	6.9532D-18	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
6.60	2.0379D-12	2.0838D-17	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
6.80	3.4700D-12	5.6164D-17	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
7.00	5.3149D-12	1.3607D-16	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
7.20	7.3776D-12	2.9843D-16	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
7.40	9.3836D-12	5.9865D-16	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04
8.01	1.2872D-11	3.2145D-15	0.0000D+00	0.0000D+00	0.0000D+00	0.0000D+00	5.0000D-04

NOTE : 'T.D.' MEANS TOTAL DISSOLVED.

NOTE : ALL MOLES/L AND MG/L VALUES ARE CONCENTRATIONS AS OPPOSED TO ACTIVITIES.

NOTE : A CONCENTRATION OF 0 CAN MEAN EITHER THE T.D. CONCENTRATION WAS 0 OR THE SPECIES CONCENTRATION WAS APPROACHING 0.